Mechanochemical Synthesis of Functional Complex Oxides and Fluorides Fine Particles(メカノケミカル法を利用した酸化物・フッ化物系機能性微粉末の合成)

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論文内容要旨

Complex oxides and fluorides fine particles, as a large group of crystalline ceramics, have a possiblity of wide applications, such as electrode materials, fuel cells, catalysts, optical materials and a like, due to their unique properties. It is well recognized that the properties of these compounds are exceedingly associated with their synthesis methods. In other word, the property of product depends on its production process. There have been several methods for synthesizing complex oxides and fluorides: one is solid-state reaction method at high temperature and the other chemical solution method, such as hydrothermal and sol-gel processes. These methods are excellent but have inherently drawbacks, such as complicated process. The solid-state reaction method is a simple operation with the use of starting solid materials, but the products are often of large particle sizes and of limitation in chemical homogeneity. As for the complex fluorides synthesized by solid-state reaction or chemical solution methods, the both processes have high risk potentially due to the use of HF gas. There has been a growing demand for developing an alternative easy and safety method, which covers high efficiency. One of the methods would be a mechanochemical route using a high-energy ball mill. This has been proven to be versatile in synthesizing materials. The most advantageous point in the mechanochemical route is non-thermal solid state reaction through structurally unstable state and physicochemical changes.

This thesis has dealt with the mechanochemical synthesis of complex oxides and fluorides fine particles. This has been discussed on dependency of reaction regarding the physic-chemical characters of starting materials as well as the features of these mechanochemical reactions.

The 1st chapter dealt with the background and the purpose of this work. Regarding a comprehensive explanation of this investigation described above, the properties of complex oxides and fluorides and their synthesis methods have been overviewed briefly. Subsequently, a novel mechanochemical method for synthesizing oxides and fluorides complexes has been introduced based on the research on the features and effects

of mechanochemical treatment. Then, the purpose of this research and content of this thesis have been also described.

The 2nd Chapter has dealt with mechanochemical synthesis of perovskite-type compounds, $LaMO_3$, through the solid-state reaction between La_2O_3 and M_2O_3 (M=Al, Ga, Fe, Cr, Y, In) powders using a planetary ball mill. It has been found that the reactivity between the two has high dependency on the crystal structure of M_2O_3. The investigated oxides, M_2O_3, are categorized into two groups: one is the corundum structure and the other the non-corundum one. Under the experimental conditions, it can be found that the oxide with non-corundum structure reacts easily with La_2O_3 by their co-grinding at room temperature to form the corresponding compounds. On the contrary, none of such reactions occur for the oxides with corundum structure. The results are shown in Table 1. To explain these phenomena, M_2O_3 itself was ground and it has been found that phase transformations from loose packing of atoms to close packing of atoms are taken place. This means that the non-corundum structure of M_2O_3 has a high reactivity with other like La_2O_3. From these experiments, it is recognized that preparation of suitable starting samples for designing a specific reaction is very important. Through the investigation on the mechanochemical reactivity of hydrous chromium oxide, obtained by heating hydrous chromium hydroxide ($Cr(OH)_3.nH_2O$) at different temperature, with La_2O_3, it is found that the hydrous oxide exhibits high reactivity compared to crystalline oxide corundum structure, due to its amorphous like of crystal structure. The obtained $LaMO_3$ powder samples consist of agglomerates with fine grains of nanometer size. The values of specific surface area vary from 5 to 12 m^2/g.

Tab. 1 Crystal structures of M_2O_3

Corundum structure (not react with La_2O_3)	Non-corundum structure (react with La_2O_3)
α-Al_2O_3	γ-Al_2O_3 (cubic)
α-Fe_2O_3	γ-Fe_2O_3 (tetragonal)
α-Cr_2O_3	β-Ga_2O_3 (monoclinic)
α-Ga_2O_3	Y_2O_3 (cubic)
	In_2O_3 (cubic)
	Mn_2O_3 (cubic)

The 3rd Chapter has dealt with the mechanochemical synthesis of $LaFeO_3$. Although the crystal structures of starting oxides play a significant role to cause mechanochemical reaction to form perovskite-type oxides, $LaMO_3$. Further investigation shows that crystal structure is important but it is not only the crucial factor to control the reactivity. This implies that another important factor is crystallite size, which plays a significant role to influence a mechanochemical reaction. In this chapter, the mechanochemical reactions between γ-Fe_2O_3, α-Fe_2O_3 and La_2O_3 have been investigated. As a result, γ-Fe_2O_3 can react with La_2O_3 mechanochemically, whereas α-Fe_2O_3 cannot. However, it is found that even in a stable corundum structure, when α-Fe_2O_3 sample with crystallite size less than 20nm is used, the mechanochemical reaction occurs easily, leading to synthesis of $LaFeO_3$. The reaction tends to be difficult with the increase in crystallite size of Fe_2O_3. In addition, the possibility of synthesizing other rare earth and iron complex oxides, $RFeO_3$ (R = Nd, Pr, Sm) has been confirmed.

The 4th chapter has dealt with the mechanochemical reaction between ammonium fluoride ($(NH_4)F$) and gallium fluoride trihydrate ($GaF_3 \cdot 3H_2O$) at 3:1 in molar ratio, by their co-grinding the mixture at room temperature using the planetary ball-mill. As shown in Figure 1, it is found that a single phase of ammonium hexafluorogallate ($(NH_4)_3GaF_6$) can be simply synthesized after 10 min in the operation even at 300 rpm in

rotational speed of the mill. At the same time, the water in hydrated GaF_3 is remained as the absorption water in the ground sample. In addition, the morphology of particles synthesized look smooth surface with good shape, comparing to other particles synthesized by grinding. This may be due to the reaction caused by low speed of grinding resulting in less damage in the particles by balls impact. Therefore, the method exhibits the advantage of operation and allows the use of hydrated GaF_3. Other alkali hexafluorogallate (K_3GaF_6, Na_3GaF_6, Li_3GaF_6) can also be synthesized by the proposed method from the grinding the constituent components (AF and $GaF_3 \cdot 3H_2O$). When the alkali fluoride has a high solubility, its mechanochemical reactions with hydrated GaF_3 can be easily performed.

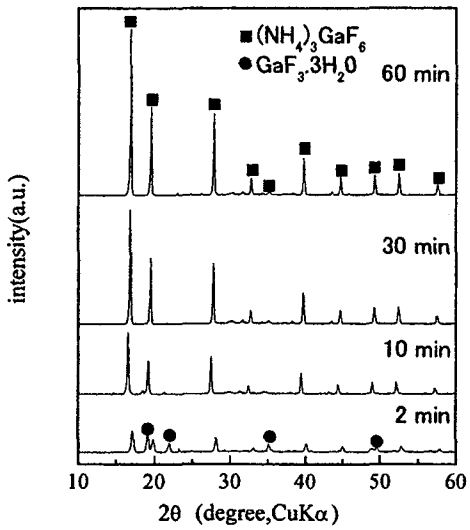

Fig.1 XRD patterns of the mixture of NH_4F and $GaF_3.3H_2O$ ground for different time at the radio 3:1

The 5th chapter has dealt with mechanochemical synthesis of complex fluorides ARF_4 (A=Li,Na,K, R=rare earth ion) from AF and RF_3 powders at room temperature using the planetary ball mill. The reactions proceed with an increase in grinding time and have been completed by 4 h. According to the transmission electron microscope (TEM) observation, the synthesized ARF_4 powders consist of agglomerates of nano-sized primary particles, which exhibit moderate water solubility. Calcining the ground product enables us to increase the particle sizes, so that the water solubility is inhibited.

The 6th chapter has dealt with the synthesis of nitrogen (N) dope zinc oxide by co-grinding the mixture of zinc oxide (ZnO) and urea ($CO(NH_2)_2$), followed by calcining the ground sample at low temperature. Compared with a method for mechanical mixing operation of the samples, the proposed method shows the formation of weak doping N into ZnO. This effect facilitates the doping of N into the oxide by calcing the ground sample at 400 ℃, which is low temperature in comparison with the usual case. In fact, the heating at 400℃ does not occur any doping of N in ZnO_2. The two-step process including grinding and calcining the sample mixture offers nonmental-element doped oxide. As shown in Figure 2, the UV-Vis spectra have shown to shift towards a lower energy side and the edge border of band gap shifts to the visible region. In the meantime, the prepared sample exhibits agglomeration of fine particles, and shows high photocatalytic ability in antibacterial test.

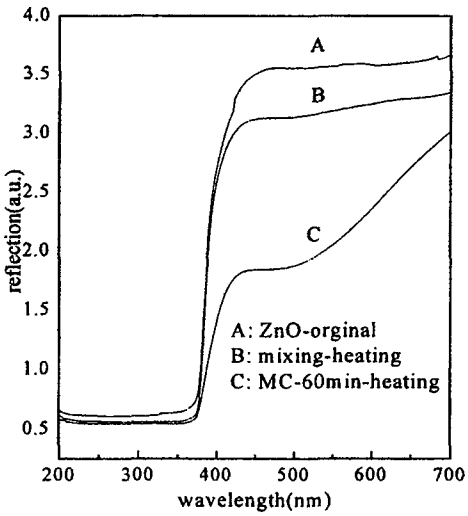

Fig.2 Optical reflection spectra of the annealed products of the mixture of ZnO and 5% urea ground for different times

The final chapter (7th) is the summary of the present thesis, and is composed of the conclusions obtained in the each chapter.

In this thesis, novel synthesis methods based on mechanochemical treatment have been proposed and their applicabilities for the complex oxides and fluorides fine particles have been introduced in this work. The investigations on the mechanochemical reactivity between corresponding oxides or fluorides show that the physic-chemical properties of starting materials play an important role in these processes. Several control parameters for synthesizing the target materials have been shown.

論文審査結果の要旨

粉体は、通常、高温固相反応法、液相法、気相法で合成されるが、そこで合成される粉体の特徴は、結晶性が良く、複数種類の元素からなる場合はそれらの組成は熱力学で既定される比になる。合成粉体の特性は優れる一方、従来の特性を超える新規特性を持つ物質を合成する場合、従来法には無い組織、組成、ランダム性・構造の無定形化などが望まれる。これを達成する手法として、メカノケミカル(MC)法があるが、この手法が、複合酸化物合成での出発原料の結晶構造依存性や、構造水・結晶水を持つ物質の固相反応についての情報は少ない。更に、金属酸化物への非金属元素のドーピングと他の物質との固相反応に及ぼす影響に関する情報も不足している。

そこで、本論文は、MC法を利用した粉末合成とドーピングに関する研究であり、全編7章より成る。

第1章は緒論であり、過去に提案された粉体合成法を整理し、その特徴を述べ、新しい特性を引き出す上ではランダム構造や非晶質組織を持つ物質を合成する必要を述べ、それを達成できるのはMC法であることを指摘。その上で、MC法の特徴、過去の実施例を挙げ、未解決事項について触れた。それを踏まえて、本論文の構成と、各章での検討結果を述べた。

第2章は、MC法によるペロブスカイト型酸化物微粉体の合成に及ぼす出発原料の結晶構造の影響について検討した結果を述べている。すなわち、出発原料には、La_2O_3を用い、これを固定し、もう一方の試料として、コランダム構造と非コランダム構造の2グループの原料粉末試料を準備し、遊星ミルを用いて乾式混合粉砕（MC処理）を行い、処理物を各種の材料科学的評価装置を用いて検定した。その結果、La_2O_3は、コランダム構造の試料とは反応しにくく、非コランダム構造の試料と反応しやすいという一定の傾向があることを見出した。

3章では、コランダム構造物質を固定し、その結晶子サイズを種々変化させた粉末試料を準備し、これとLa_2O_3とのMC処理を行い、果たしてコランダム構造物質はどんな結晶子サイズでも反応性が良くならないのかについて検討した。その結果、結晶子サイズが20nm程度以下になると反応性は良くなることが判明した。この知見は重要であり、たとえ安定なコランダム構造物質でも結晶子サイズを加熱法や粉砕法で制御できれば、MC固相合成が達成できる事を意味する。

第4章は、GaN単結晶育成のための前駆体$(NH_4)_3GaF_6$を$GaF\cdot 3H_2O$と$(NH_4)F$のMC処理により合成する場合の$GaF\cdot 3H_2O$中の水分子の影響を検討している。その結果、MC合成には、結晶水へのFならびに(NH_4)イオンの溶解度が重要であることを示唆し、$(NH_4)_3GaF_6$が固相合成できる反応機構を提案している。

第5章は、第4章で示唆した反応機構を確認するための検討であり、水に対する溶解度の異なる3種類のフッ化アルカリ（LiF、NaF、KaF）を準備し、La_2O_3とのMC反応を実験によって確認し、その結果とフッ化アルカリの溶解度と関連性を検討している。その結果、やはりフッ化物の結晶水への溶解性が高いほどMC固相反応が進行するという仮説の妥当性を確認している。

第6章では、MC法の新しい素材合成への活用を目指し、ZnOと尿素のMC処理と低温加熱法を組み合わせたZnOへのNドーピングに関する実験的検討結果を纏めている。ZnOへのNドーピング量は、尿素添加率やMC処理時間によって変化でき、また、MC処理後400℃という低温度での焼成でNドーピングが達成できる事を明確にした。

第7章は、結論であり、各章の結言を纏めた。

以上、本論文は素材工学、地球工学の発展に寄与するところ少なくない。よって、本論文は、博士(工学)の学位論文として合格と認める。